Characterization of Structure and Transport of Cathodically Electrodeposited Thin Films of Nickel Hexacyanoferrates

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Thin films of Nickel Hexacyanoferrate (NiHCF), analogues of Prussian Blue, have been shown to be useful for electrochemical ion sensing[1-4] as well electrochemical ion exchange.[5-6] The films function by transport of alkali cations into and out of their structure upon modulation of the matrix potential. We have shown that the redox reaction can be represented as

$$A_{1.33}Ni^{II}_{1.33}Fe^{II}(CN)_6 - xe^- - xA^+ \leftrightarrow A_{1.33-x}Ni^{II}_{1.33}Fe^{II+x}(CN)_6$$

where A is an alkali cation and x is the fractional oxidation state of iron.[7]

Raman spectroelectrochemical experiments are used to probe NiHCF's cyanide bond, which is sensitive to the oxidation state of the coordinated metal atom (Fe).[8] We use both *in-situ* and *ex-situ* Raman spectroscopy of the cyanide bond to characterize the redox switching of NiHCF intercalated with Na^+, K^+, and Cs^+ cations. Multivariate analysis is used to quantify trends in the Raman spectral data. Dynamic electrochemical and Raman measurements are also used to probe diffusivities of the different intercalated cations.

Understanding ion transport in these materials also requires knowledge of their structure. Therefore, we are working with analytical techniques that probe both local and long range order. Extended x-ray absorption fine structure (EXAFS) is used to probe the local environment around the Ni and Fe atoms in hopes of resolving, among other characteristics, the atom's coordination number. A complimentary technique to EXAFS is x-ray diffraction, which is used to study the long range order of the crystal structure. Several NiHCF samples, including both oxidized and reduced films as well as films loaded with different cations, are being studied using these techniques. The structural methods, in conjunction with detailed knowledge of the redox switching of the film via Raman spectroscopy, have helped create a more accurate picture of NiHCF.

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